



Calorimetric study of hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$



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ABSTRACT

For the first time hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$ was studied by means of calorimetric method with applying of the Tian–Calvet type calorimeter at 200 and 250 °C. The processes of hydrogen absorption and desorption were carried out and pressure–composition isotherms for the $\text{Sm}_2\text{Fe}_{17}\text{—H}_2$ system and enthalpy change with hydrogen concentration in the metallic matrix were obtained. On the base of collected data supposition about order of filling the interstitial site by hydrogen atoms was made.

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1. Introduction

$\text{Sm}_2\text{Fe}_{17}$ nitride is a perspective material for production of permanent magnets possessing excellent magnetic properties. The process of $\text{Sm}_2\text{Fe}_{17}$ hydrogenation is a constituent part of the $\text{Sm}_2\text{Fe}_{17}$ nitride preparation [1–6]. However till now this process is not studied completely. Generally scientists studied magnetic properties [7–9] and influence of hydrogen on the $\text{Sm}_2\text{Fe}_{17}$ structure. It has been established that hydrogen atoms occupied completely 9e-interstices and partially 18g-interstices in the crystal structure of $\text{Sm}_2\text{Fe}_{17}$ [10]. But there are few thermodynamic properties which could confirm this phenomenon. In works [11,12] partial molar enthalpies and entropies of the reaction of hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$ were determined from the pressure–composition isotherms. According to the data presented in Fig. 2 in the work [11] in the region of hydrogen concentration $0.5 < C < 2.6$ the values of enthalpy of absorption reaction change approximately from -17 to -14 kcal/mol H_2 (or from -71.18 to -58.62 kJ/mol H_2 if these values are recalculated in terms of SI units, Le Système International d'Unités). Japanese researchers presented in [12] the calculated data of the enthalpy of hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$ in the functional form $\Delta H = f(C)$ where ΔH – the relative partial molar enthalpy, $C = H/\text{Sm}_2\text{Fe}_{17}$ (see Fig. 2 in the work [12]). And how one can see from this plot the enthalpy values change from approximately -45 to -27 kJ/mol H

in the range $0.1 < C < 4.5$. Cuevas et al. [13] studied hydrogen desorption from $\text{R}_2\text{Fe}_{17}\text{H}_x$ ($\text{R}=\text{Nd}$ and Dy) compounds with $x \leq 5$ using differential scanning calorimetry (DSC) and they determined that the heat of hydrogen desorption is 29.2 ± 0.8 kJ/molH for both studied compounds.

In the present work the $\text{Sm}_2\text{Fe}_{17}\text{—H}_2$ system was studied by calorimetric method with applying of differential heat-conducting calorimeter of Tian–Calvet type.

2. Experimental

The original $\text{Sm}_2\text{Fe}_{17}$ sample was melted in the induction furnace the stoichiometric mixture composed of its metals 2–17 (25.4% Fe and 73.6% Sm) in argon atmosphere (1–1.5 atm). Purity of initial materials was Fe – 99.999% and Sm – 99.98%. The obtained ingot was annealed in the sealed quartz vessel in the vacuum resistance furnace at 1100 °C for 40 h to ensure homogeneity.

X-ray powder diffraction analysis of the initial $\text{Sm}_2\text{Fe}_{17}$ sample and the hydrogenated product of the initial sample obtained after completion of the calorimetric study were carried out on the Rigaku Ultima IV diffractometer (Cu $K\alpha$ -radiation, graphite monochromator). The refinement of diffraction patterns and determination of unit lattice parameters were carried out using set of programs PDXL.

The chemical composition of the initial sample was determined by a roentgen fluorescent analysis on spectrometer Rigaku Primus II and X-ray spectrography microanalysis with a scanning electron microscope JEOL JSM-6610 LV.

The study of hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$ was carried out by calorimetric method. The twin-cell heat-conducting calorimeter Tian–Calvet type connected to conventional Sievert's-type volumetric apparatus for gas dosed feeding was applied for this purpose. The apparatus scheme, experimental procedure and analysis of the collected data were described elsewhere [14]. The use of such a complex installation permits to measure $P\text{—}C\text{—}T$ and $\Delta H\text{—}C\text{—}T$ (P – equilibrium pressure, C – hydrogen concentration in the IMC, $C = H/\text{Sm}_2\text{Fe}_{17}$, T – experimental temperature, ΔH – reaction enthalpy) simultaneously. A purity of hydrogen used at hydrogenation was 99.9999%.

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3. Results and discussion

3.1. X-ray analysis

According to data of carried out analysis the initial sample $\text{Sm}_2\text{Fe}_{17}$ after heat treatment contained 95% $\text{Sm}_2\text{Fe}_{17}$, 4% SmFe_3 and less than 1% $\alpha\text{-Fe}$. The lattice parameters of the initial sample were $a - 8.5594(2) \text{ \AA}$, $b - 8.5594(2) \text{ \AA}$, $c - 12.4517(6) \text{ \AA}$, $V - 790.03 \text{ \AA}^3$. After completion of the calorimetric experiments the sample under investigation was evacuated at $350 \text{ }^\circ\text{C}$ during 4 h, cooled to room temperature and hydrogenated at hydrogen pressure 40 atm. The amount of absorbed hydrogen was estimated using a volumetric method as stated in [14]. The chemical composition of hydrogenated sample was $\text{Sm}_2\text{Fe}_{17}\text{H}_{4.7}$. X-ray data showed that $\text{Sm}_2\text{Fe}_{17}\text{H}_{4.7}$ was single-phase compound with the following lattice parameters: $a - 8.6818(4) \text{ \AA}$, $b - 8.6818(4) \text{ \AA}$, $c - 12.5576(9) \text{ \AA}$, $V - 819.70(8) \text{ \AA}^3$, that agrees with reference data [4,7,12]. A volume of unit cell increased on 3.6% during hydrogenation. Such as X-ray analysis was carried out after completion of the calorimetric investigation (after 20 cycles of absorption/desorption connected with processes evacuated of the sample under investigation at $350 \text{ }^\circ\text{C}$ during 4 h which carried out before each experiment) two conclusions could be made: (1) during study the initial sample was not undergone disproportionation, (2) the additional homogenization of the sample took place.

3.2. P - C - T relationships

The hydrogen absorption and desorption by $\text{Sm}_2\text{Fe}_{17}$ were studied at 200 and $250 \text{ }^\circ\text{C}$. In Fig. 1 desorption isotherms were shown for both temperatures. Fig. 2 shows the absorption and desorption

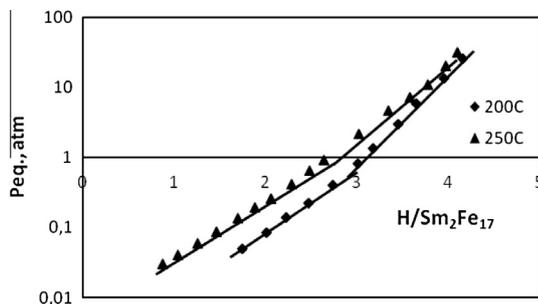


Fig. 1. Desorption isotherms for $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ at 200 and $250 \text{ }^\circ\text{C}$.

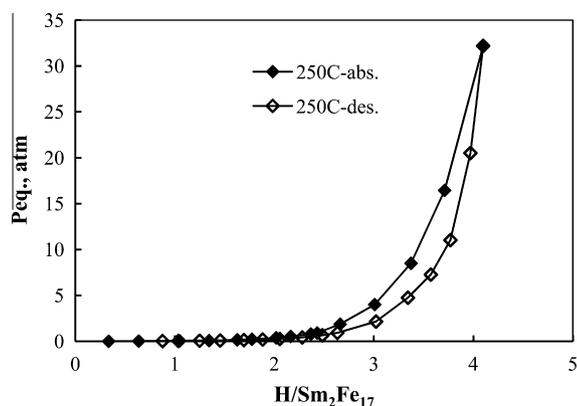


Fig. 2. Absorption and desorption isotherms for $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ at $250 \text{ }^\circ\text{C}$. Filled symbols refer to absorption of H_2 and open symbol to desorption.

isotherms obtained at $250 \text{ }^\circ\text{C}$. Obviously in plots of the dependence $P = f(C)$ (Fig. 1) we could not mark the plateau region which is characteristic property when hydride IMC forms.

However at the same time Fig. 2 shows that the hydrogen absorption and desorption isotherms at $250 \text{ }^\circ\text{C}$ do not coincide (in region $1.5 < C < 3.5$). In other words there is small hysteresis of pressures. The similar phenomenon for rising branch of isotherm in the $\text{AB}_2\text{-H}_2$ systems was described in the works [15,16] for the $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{-H}_2$ and ZrCrFe-H_2 systems. Thus obtained data permit to assume that in the $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ system at $250 \text{ }^\circ\text{C}$ hydrogen absorption takes place as two-stage process.

Some peculiarities of desorption isotherms collected at 200 and $250 \text{ }^\circ\text{C}$ were noted. Namely in plots of the dependences $P = f(C)$ the inflection points may be marked (Fig. 1). At $200 \text{ }^\circ\text{C}$ this point disposes to in the region of hydrogen concentration $C \approx 3.0$ whereas at $250 \text{ }^\circ\text{C}$ this one is situated in the region of $C \approx 2.1$. Similar observations were made in the works [15,17–19] for other IMC- H_2 systems.

3.3. Calorimetric results

Figs. 3a, b and 4a, b show dependences of partial molar enthalpy of hydrogen absorption/desorption change at 200 and $250 \text{ }^\circ\text{C}$.

In Fig. 3a the plot of $|\Delta H_{\text{abs.}}|$ - C dependence at $200 \text{ }^\circ\text{C}$ is presented. In the initial region ($C \approx 0.5$) $|\Delta H_{\text{abs.}}| = 88 \text{ kJ/mol H}_2$. Then one can select two regions $0.8 < C < 1.6$ and $1.8 < C < 2.6$ where the enthalpy values equal $-80.2 \pm 0.8 \text{ kJ/mol H}_2$ and $-74.9 \pm 2.2 \text{ kJ/mol H}_2$. Further increase of hydrogen concentration in the metallic matrix leads to sharp reduction of the enthalpy values in magnitude to 31 kJ/mol H_2 . For hydrogen desorption at $200 \text{ }^\circ\text{C}$ the similar picture is observed (Fig. 3b). At hydrogen concentration $1.2 < C < 1.6$ $\Delta H_{\text{des.}} \approx 81 \text{ kJ/mol H}_2$.

Such as in the $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ system equilibrium hydrogen pressure sharply decreases with decreasing of hydrogen content then we could not study hydrogen desorption at hydrogen concentration $C < 1.2$ that was connected with possibilities of applied devices. In the part $1.6 < C < 2.6$ the plot has a small slop (from 76 to 72 kJ/mol H_2), $\Delta H_{\text{des.}} = 73 \pm 1.1 \text{ kJ/mol H}_2$, further the enthalpy values begin to reduce sharply from 70 (at $C \sim 2.9$) to 30 kJ/mol H_2 (at $C \sim 4.0$).

Fig. 4a shows the plot of the dependence $|\Delta H_{\text{abs.}}|$ - C at $250 \text{ }^\circ\text{C}$. The rise of experimental temperature leads to some change in thermodynamics of this process. In the plot of $|\Delta H_{\text{abs.}}|$ - C one can select three parts: $0.3 < C < 2.0$, $|\Delta H_{\text{abs.}}| = 81.7 \text{ kJ/mol H}_2$, $2.1 < C < 3.0$ $|\Delta H_{\text{abs.}}| = 75.6 \text{ kJ/mol H}_2$ and $3.0 < C < 4.0$ where the partial molar enthalpy values sharply decrease in magnitude to $\sim 35 \text{ kJ/mol H}_2$.

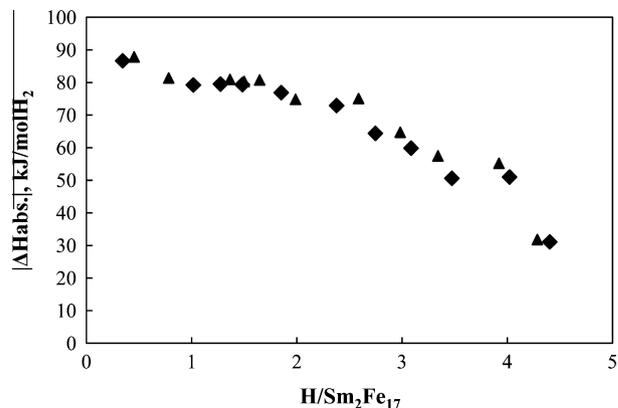


Fig. 3a. Absorption enthalpy vs. composition at $200 \text{ }^\circ\text{C}$ for $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$. The different symbols refer to different series of determinations.

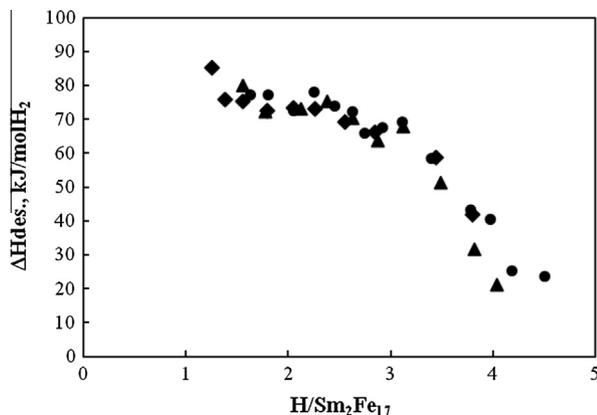


Fig. 3b. Desorption enthalpy vs. composition at 200 °C for $\text{Sm}_2\text{Fe}_{17}\text{--H}_2$. The different symbols refer to different series of determinations.

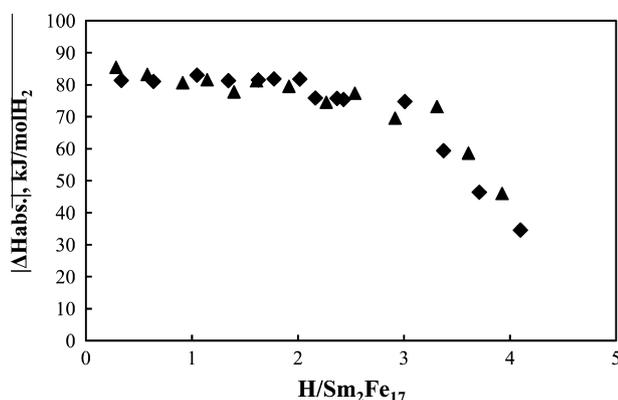


Fig. 4a. Absorption enthalpy vs. composition at 250 °C for $\text{Sm}_2\text{Fe}_{17}\text{--H}_2$. The different symbols refer to different series of determinations.

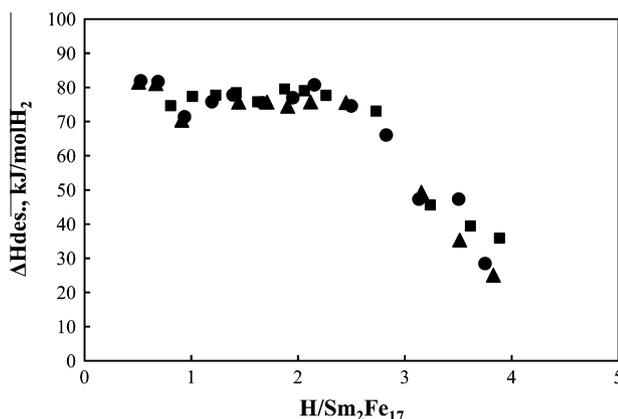


Fig. 4b. Desorption enthalpy vs. composition at 200 °C for $\text{Sm}_2\text{Fe}_{17}\text{--H}_2$. The different symbols refer to different series of determinations.

In Fig. 4b the plot of the $\Delta H_{des.} = f(C)$ dependence is presented for 250 °C. This plot shows that in the region of low hydrogen concentration ($0.5 < C < 0.7$) $\Delta H_{des.} \approx 82 \text{ kJ/mol H}_2$ then there is the part ($1.0 < C < 2.3$) where $\Delta H_{des.} \approx 76.8 \pm 0.8 \text{ kJ/mol H}_2$ and after that these ones sharply decreased.

It is known that in R_2Fe_{17} (R-light rare earth element) with the rhombohedral structure R-3m hydrogen atoms occupy octahedral 9e-interstices and 18g-interstices [7,8] moreover these interstices may be occupied by different way depending on experimental

conditions. For example in the work [12] it was determined that hydrogen atoms may occupy the 9e- and 18g-interstices only up to 500 K. Further rising of temperature leads to the fact that hydrogen occupies only 9e site. In the work [12] the authors for determination of the order of occupation by hydrogen the 9e- and 18g-interstices used data of partial molar entropy of hydrogen reaction with $\text{Sm}_2\text{Fe}_{17}$. Properly from these data the partial molar entropy of reaction decreases with rising hydrogen concentration in $\text{Sm}_2\text{Fe}_{17}$ to $C=2$. Then the entropy begins to rise and this process continues to $C=3.25$. The further increase of hydrogen concentration is accompanied by entropy decrease. The authors suppose that an acceptable explanation of phenomenon may be the fact that 18g sites may begin to fill even at relatively low hydrogen concentrations. The thermodynamic data are confirmed by sudden changes in the lattice parameters and saturation magnetization $\text{Sm}_2\text{Fe}_{17}$ with hydrogen concentration [12] that take place at $C=2.0$. However the results obtained in the work [13] are in some contradiction with foregoing cited results. In the work [13] the authors studied hydrogen desorption from $\text{Nd}_2\text{Fe}_{17}\text{H}_x$ and $\text{Dy}_2\text{Fe}_{17}\text{H}_x$ by means of DSC. Nd and Dy were chosen for study as representatives of light and heavy rare earth elements as $\text{R}_2\text{Fe}_{17}\text{H}_x$ demonstrated two different crystal structures [20–23] rhombohedral (space group R-3m, light rare earth elements) and hexagonal (space group $\text{P6}_3/\text{mmc}$, heavy rare earth elements). There are two peaks on DSC curves for the samples containing Nd at high hydrogen concentration ($x=5$) [13]. At hydrogen concentrations $x=1, 2, 3$ there is only one peak on DSC curves. It means that at low concentrations hydrogen occupies only one type of site. At $x=3$ the peak shows distinct shoulder at the low temperatures. From these data the authors concluded that hydrogen H_1 occupied pseudo-octahedral 9e-interstice and H_2 occupies the tetrahedral 18g-interstices. Authors also mark that H_1 position probably consists of two nonequivalent energetic sites what is witnessed by the shoulder on DSC curves. These reflections could be related with our case because both Sm and Nd belong to light rare earth elements and $\text{Sm}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$ have identical rhombohedral structure.

As seen from Fig. 4a there is the initial part $0.3 < C < 2.0$ on the plot of $|\Delta H_{abs.}|-C$ at 250 °C where the enthalpy values are constant. It may be assumed that the occupation of 9e-interstices took place. Then the enthalpy values slightly decrease in magnitude ($2.1 < C < 3.0$). Probably in this part at hydrogen absorption the structure of forming solid solution puts in order. Perhaps later on occupation of 9e-interstices occurs but energy of hydrogen atoms bond with metallic matrix decreases [13]. That is at 250 °C we obtained two values of enthalpy reactions what could be related to the presence of two non-equivalent energy sites [13]. On the next stage of hydrogen absorption enthalpy values sharply decrease what evidently correlates to the occupation by hydrogen 18g-interstices only.

At the hydrogen absorption took place at 200 °C as probably at 250 °C the 9e interstices are occupied at first but the plot of $|\Delta H_{abs.}|-C$ presented in Fig. 3a permits to make assumption that at $C=2.6$ 18 g-interstices already begin to occupy as values of partial molar enthalpy of hydrogen absorption sharply decrease in magnitude.

4. Conclusions

For the first time the measurements of heat effects of absorption/desorption reaction of hydrogen in the $\text{Sm}_2\text{Fe}_{17}\text{--H}_2$ system were carried out by means of calorimetric method using the calorimeter of Tian–Calvet type, the values of the partial molar enthalpies of the absorption/desorption reaction were obtained. On the base of the collected data the conclusion was made that

at absorption taking place at 200 °C, probably, such as at 250 °C 9e interstitial sites were occupied the former. As one can see from Fig. 3a it can be assumed that at $C = 2.6$ already the 18g interstitial sites start were occupied as the values of the partial molar enthalpy of hydrogen absorption sharply decrease in magnitude.

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